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Temperature dependence of external modes of water in infrared spectra of monohydrates of some divalent transition metal sulfates

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The IR spectra of $MSO_4.H_2O$ (M=Mn, Co, Ni) which are isomorphous have been recorded in the region 1000-250 cm^{-1} at liquid nitrogen temperature (LNT). The overlapping contours have been analyzed into Lorentzian components and the positions half-widths and integrated intensities have been reported for different components of external modes of water. All components show an increase in intensity and a shift towards higher frequency at LNT over their room temperature (RT) values. In the region around 300 cm^{-1} one dominant temperature sensitive band is attributed to M-O_w stretch. Correlation curves are given for H_2O (rock), H_2O (Wag) and M-O_w stretch frequency against M-O_w distances.

1. INTRODUCTION

The hydrates $MSO_4.H_2O$ (M=Mn, Co, Ni) are isostructural belonging to the space group C^6_{2h} having four formula units per unit cell[1,2]. Infrared studies of these salts have been reported in the past[3,4] at room temperature (RT) above 600 cm^{-1}. In a previous paper by the authors[5] an analysis of the overlapping bands with half widths and relative integrated intensities of the internal and librational modes of water along with the internal modes of SO_4^{2-} at room temperature were reported and a linear correlation of the frequency of the rocking mode of H_2O with M-O_w distance was given, O_w being the oxygen of the water. In the present paper the effect of changing the temperature from room temperature to liquid nitrogen temperature (LNT) on the water librational and M-O_w stretch bands is presented, and the correlation with M-O_w distance is extended to H_2O wag and M-O_w stretching frequencies (at LNT) also.

2. Experimental

The monohydrates of Mn and Co salts were prepared by crystallization from aqueous solution at ~ 80°C and drying the precipitate in an oven at 100°C, while that of Ni was prepared by baking the hexahydrate at ~ 120°C. The hydration level was checked by the weight loss method. Spectra were recorded in Nujol mull on Perkin-Elmer 521 spectrophometer. For low tehperatures (LT) a modified Wagner Hornig type cell was used, which could be directly inserted in the sample beam without any material change of the optical path. Prior to cooling the cell was evacuated to ~ 10^{-5} cm of Hg. The temperatures were measured by a thermocouple and the spectra at different temperatures were recorded without disturbing the geometry.

3. Results and Discussion

(a) *Analysis of the Spectra*

Figure 1 gives the spectra in region 250-1000 cm^{-1} at RT and LNT for the three salts. Considerable overlapping of the bands will at once be observed. The contours were subjected to analysis into Lorentzian components, which is justified when band widths are much larger than instrumental resolution. The

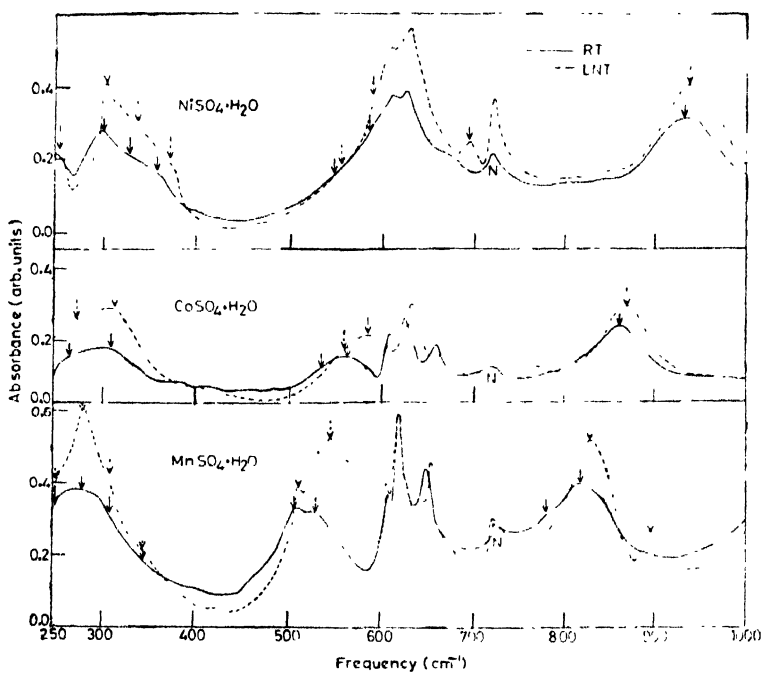

Fig. 1. Infrared absorption spectra at room temperature (RT) and Liquid Nitrogen Temperature (LNT) of (a) $MnSO_4.H_2O$ (b) $CoSO_4.H_2O$ (c) $NiSO_4.H_2O$ in Nujol mull. N denotes bands due to nujol.

basis was to fit the minimum number of components warranted by the observed contours and in most cases the positions were reproducible within 5 cm^{-1} and intensities within 10%. In those cases where the choice was between one component slightly departing from Lorentzian shape and two components with good Lorentzian shapes the first was preferred, unless there was other evidence favouring the second alternative. Figure 2 gives the typical resolution of a contour into Lorentzian components in the latter category. In the cases of Co and Mn salts the SO_4^{2-} (ν_1) bands have Lorentzian shapes and two water librations are found well separated. Hence in this spectrum of Ni salt the SO_4^{2-} bands were kept in Lorentzian shapes and the residue led necessarily to two components on the lower frequency tail.

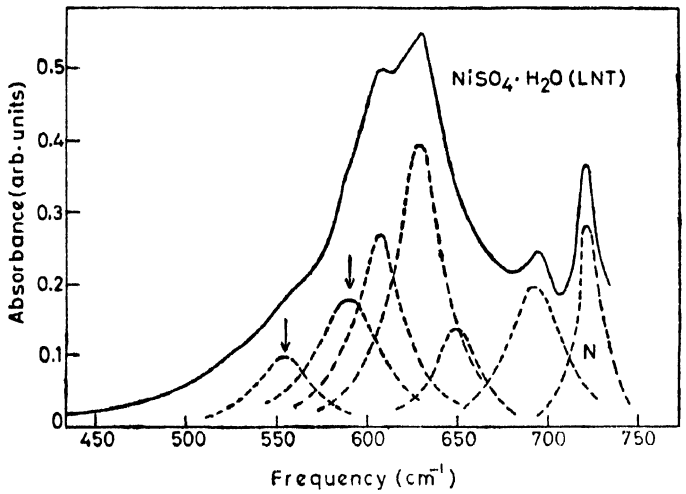

Fig. 2 Typical analysis of the absorption band contour in the region 500-750 cm^{-1} (solid curve) into Lorentzian components (broken curves) for $NiSO_4.H_2O$ spectrum LNT. The water wagging components at low frequency tail are marked by arrows

Table 1 gives the results of analysis excluding the internal modes of SO_4^{2-}. Band positions, half widths and integrated intensities are given.

(b) Librational Modes of Water

Amongst the librational modes of water, the rocking mode has lowest frequency 820 cm^{-1} in the Mn salt which increases to 860 cm^{-1} in the Co salt and 930 cm^{-1} in the Ni salt. In all the three cases the lowering of temperature results in an increase in peak intensity and shift towards higher frequency. The observed curves cannot be resolved into components in the case of Co and Ni salts but in the case of Mn salt the contour shows the presence of an additional component at both RT and LNT. In this spectrum a new sharp band ($\Delta\nu_{\frac{1}{2}} = 20$ cm^{-1}) appears at 892 cm^{-1} at LNT. Spectra

Table 1. Infrared absorption bands of external modes of water of monohydrates of Mn, Co and Ni sulfates at room temperature (RT) and at liquid nitrogen temperature (LNT)

$MnSO_4.H_2O$						$CoSO_4.H_2O$						$NiSO_4.H_2O$						Assignment
RT			LNT			RT			LNT			RT			LNT			
ν	$\Delta\nu_{\frac{1}{2}}$	I	ν	$\Delta\nu_{\frac{1}{2}}$	I	ν	$\Delta\nu_{\frac{1}{2}}$	I	ν	$\Delta\nu_{\frac{1}{2}}$	I	ν	$\Delta\nu_{\frac{1}{2}}$	I	ν	$\Delta\nu_{\frac{1}{2}}$	I	
			892*	20	2													?
820	80	25	830	50	28	860	80	20	865	80	23	930	100	25	935	100	40	H_2O Rock
770	60	8	790	50	5													
															695*	35	7	?
530	80	16	547	70	35	560	80	10	585	60	12	585	40	6	590	40	7	H_2O Wag
510	30	6	510	20	2	535	40	2	560	30	2	545	40	3	555	40	3	
345	40	3	345	40	4							360	40	6	374	24	3	
310	40	5	310	50	6													
290*	80	25	290*	50	28	310*	80	13	315*	80	20	325*	30	3	338*	40	10	M-O_4 Stretch
												302	40	10	304	30	10	
250	30	2	250	40	6	265	40	3	275	40	5	250	30	6	254	20	4	

ν = Position of the band, $\Delta\nu_{\frac{1}{2}}$ = Full band width at half the intensity
I = Integrated Intensity, * = Temperature dependent.

at intermediate temperatures show that this band appears suddenly at ~ —100°C and increases in intensity as the temperature is progressively lowered to LNT. The origin of this band is at present not clear.

The wagging mode region also has frequencies in the increasing order Mn → Co → Ni. One result of this is that while this region is well separated from the region of ν_4 of SO_4^{2-} in the Mn salt it penetrates into the tail of the ν_4 region of SO_4^{2-} in the case of Ni salt. The main wagging component in RT spectra falls at 530, 560 and 585 cm^{-1} in Mn, Co and Ni salts respectively. At LNT each of them shifts by about 20 cm^{-1} towards higher frequency and also increases in intensity. A low frequency component occurs at 510 cm^{-1} in the Mn salt, not shifting with change of temperature. The analysis of the corresponding bands in Co and Ni salts is less certain due to heavy overlaping. At low temperature a band at 695 cm^{-1} appears distinctly in the Ni salt. If the corresponding band exist for the Mn and Co salts, they would fall in the region of ν_4 of SO_4^{2-} and would not be oyserved because of overlapping.

(d) M-O Stretching

In the region around 300 cm^{-1} there are four components for Mn and Ni salts and two in the case of Co salt at RT. As there are three types of oxygens (O_1 and O_2 of the sulfate group and O_w of the water) and three different M-O distances in the coordination octahedra around M,[1][2] one would expect three bands due to M-O stretch in this region. Besides these, bands due to combination with low lying lattice modes can also occur. It is noticed that one component (falling at 290, 310 and 332 cm^{-1} in case of

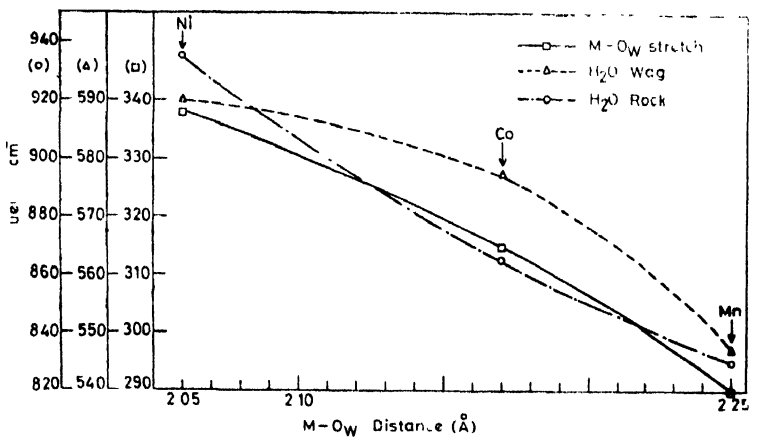

Fig. 3. Correlation of IR Frequencies at LNT of M-O_w stretch, H_2O Wag, and H_2O Rock with M-O_w distance in $MSO_4.H_2O$ (M=Mn, Co, Ni).

Mn, Co and Ni respectively) shows the greater temperature variation in intensity or half-width while the others show marginal changes. As the

bands associated with internal modes of SO_4^{2-} are affected to much lesser degree by lowering of temperaaure, it may be inferred that the components showing marked dependence on temperature are associated with M-O_w stretch. These are also the dominana bands in the region.

(e) Correlation of Frequencies with M-O_w distances

Correlation of ν (rock) with M-O_w distances has already been reported earlier[5]. Now we find that such correlation applies also to ν (wag) and ν (M-O_w) stretch. Figure 3 gives the correlation curves using the low temperature data.

References

1 Yuvette Le Fur, Jean Coing-Boyant and Gerald Bassi. Compt. Rend| Ser C, **269**, 632 (1966).

2. H R. Oswald, Helv. Chim. Acta. **48**, 490 (1965).

3 H. R Oswald, Helv. Chim Acta, **48**, 600 (1965)

4 Claude de Rocchiccioli, Compt Rend. **257**, 3851 (1963)

5 V P Tayal, D. P. Khandelwal and H D. Bist, Solid State Physics (India) **17C**, 263 (1974).